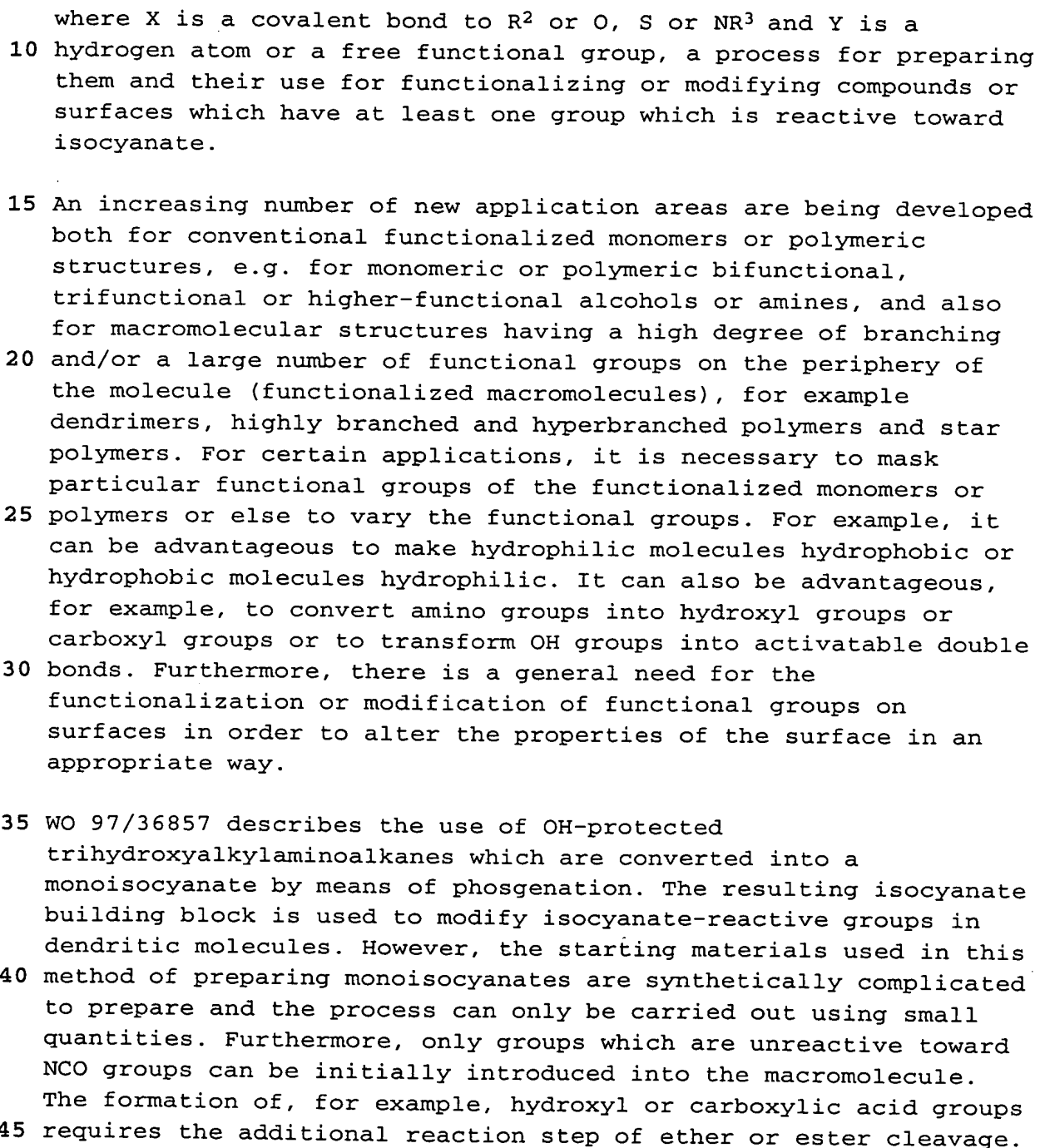


5 The present invention relates to compounds of the formula 1



## 2

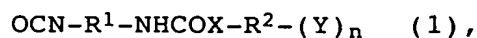
H.W.I. Peerlings and E.W. Meijer, Tetrahedron Lett. 40 (1999) 1021-1024, likewise describe the use of specially prepared alkyl monoisocyanates and aryl monoisocyanates for the surface modification of polyamine dendrimers. Here too, only groups which  
5 are unreactive toward isocyanates are introduced into the macromolecule.

Furthermore, R.M. Versteegen, R.P. Sijbesma and E.W. Meijer, Angew. Chem. 1999, 111, 3095-3097, describe the synthesis of  
10  $[\eta]$ -polyurethanes in which phosgenation of linear aliphatic  $\alpha,\omega$ -aminoalcohols is used for the in-situ generation of hydroxyisocyanates which are not stable in the reaction solution and immediately polymerize to form linear polyurethanes.

15 There is therefore a continuing need for building blocks which make it possible to functionalize or modify compounds or surfaces having isocyanate-reactive groups in any desired way.

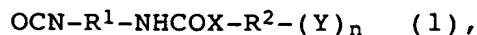
It is an object of the present invention to provide building  
20 blocks containing isocyanate groups which can be used for functionalizing or modifying compounds or surfaces having at least one group which is reactive toward isocyanate. A further object of the invention is to provide a process for preparing these building blocks.

25 We have found that this object is achieved by compounds of the formula 1



30 as described in the following text.

The present invention provides compounds of the formula 1,  
35 hereinafter referred to as building blocks,

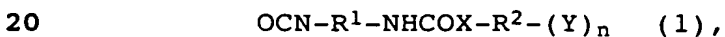


where  $R^1$  and  $R^2$  are each a substituted or unsubstituted, linear or  
40 branched, saturated or unsaturated alkylene radical having from 1 to 20 carbon atoms, preferably from 2 to 20 carbon atoms, more preferably from 4 to 20 carbon atoms and particularly preferably from 6 to 20 carbon atoms, a substituted or unsubstituted, saturated or unsaturated cycloalkylene radical having from 3 to  
45 20 carbon atoms, a substituted or unsubstituted arylene radical having from 3 to 20 carbon atoms, an arylenealkylene radical having from 4 to 20 carbon atoms, a heterocyclic radical or any

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linear or branched sequence of two or more of the radicals mentioned, if desired linked via ether, thioether, ester, amine or amide structures, X is a covalent bond to R<sup>2</sup> or O, S or NR<sup>3</sup>, where R<sup>3</sup> is a hydrogen atom or a substituted or unsubstituted, 5 linear or branched, saturated or unsaturated alkyl radical having from 1 to 20 carbon atoms, a substituted or unsubstituted, saturated or unsaturated cycloalkyl radical having from 3 to 20 carbon atoms, a substituted or unsubstituted aryl radical having from 3 to 20 carbon atoms, a heterocyclic radical or any linear 10 or branched sequence of two or more of the radicals mentioned, Y is a free functional group and n is an integer from 1 to 20, preferably from 1 to 5, particularly preferably from 1 to 3. Y can also be a hydrogen atom.

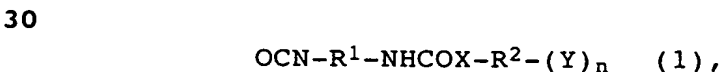
15 The invention further provides a process for functionalizing or modifying compounds or surfaces which have at least one group which is reactive toward isocyanate, by reacting a compound of the formula 1



where R<sup>1</sup>, R<sup>2</sup>, X, Y and n are as defined above, with at least one isocyanate-reactive group of a compound having at least one isocyanate-reactive group, or with at least one

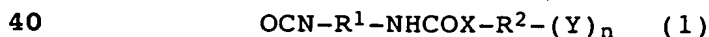
25 isocyanate-reactive group on a surface which has at least one isocyanate-reactive group.

The invention further provides for the use of a compound of the formula 1



where R<sup>1</sup>, R<sup>2</sup>, X, Y and n are as defined above, for functionalizing or modifying compounds or surfaces which have at least one group 35 which is reactive toward isocyanate.

Finally, the invention provides a process for preparing a compound of the formula 1



by reacting a diisocyanate of the formula 2



45 with a compound of the formula 3



where  $\text{R}^1$ ,  $\text{R}^2$ ,  $\text{R}^3$ , X, Y and n are as defined above and X in formula 3 can also be OCO.

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For the purposes of the present invention, a substituted alkylene radical is an alkylene radical which is substituted at at least one place by a  $\text{C}_1\text{-C}_6$ -alkyl radical, a  $\text{C}_3\text{-C}_8$ -aryl radical, a halogen atom selected from among fluorine, chlorine, bromine or  
10 iodine, or a mixture thereof. The terms substituted cycloalkylene radical, substituted arylene radical, substituted alkyl radical, substituted cycloalkyl radical and substituted aryl radical are defined analogously.

15 For the purposes of the present invention, a free functional group is a reactive position which is not protected by a protective group. Examples of free functional groups which can be used for the purposes of the present invention are hydroxyl, thiol, nitro, substituted or unsubstituted amino, amido, sulfonic  
20 acid, sulfenic acid, sulfinic acid, sulfonamide, carbonyl, carboxyl, nitrile, isonitrile, cyanate, isocyanate, thiocyanate, isothiocyanate, silyl, silanyl, substituted or unsubstituted phosphine, phosphoric acid, phosphorous acid, phosphonate, acryl, methacryl, vinyl, allyl and acetylene groups and halogen atoms.

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In the formulae, Y is preferably a vinyl, allyl, sulfonyl, sulfenyl, sulfinyl, sulfonamide, carbonyl, silyl, silanyl, hydroxy, thiol, carboxyl, sulfonic acid, acryl, methacryl or substituted or unsubstituted amino group.

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Y is particularly preferably a hydroxy, thiol, carboxyl, sulfonic acid, acryl, methacryl or substituted or unsubstituted amino group.

35 For the purposes of the present invention, a substituted amino group is an amino group which is substituted by one or two substituents selected from the group consisting of  $\text{C}_1\text{-C}_6$ -alkyl radicals,  $\text{C}_3\text{-C}_8$ -aryl radicals, halogen atoms selected from among fluorine, chlorine, bromine and iodine, and mixtures thereof.

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For the purposes of the present invention, a group which is reactive toward isocyanate (also referred to as an isocyanate-reactive group) is a group which bears hydrogen atoms which are reactive toward NCO groups or which can form an  
45 addition compound with NCO groups. Examples of such groups are OH, SH, NH, COOH groups, epoxides, acid anhydride or carbodiimide

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groups; among these, preference is given to OH, SH, NH or COOH groups.

- In a preferred embodiment of the building blocks of the present invention, R<sup>1</sup> is a 2,4-tolylene, 2,6-tolylene, 4,4'-diphenylmethylene, 2,4'-diphenylmethylene, 3-alkyl-4,4'-diphenylmethylene, where alkyl is C<sub>1</sub>-C<sub>10</sub>-alkyl, 1,3- and 1,4-phenylene, 1,5-naphthylene, tolidine, biphenylene, tetramethylene, hexamethylene, dodecylene, alkylene lysine ester where alkylene is C<sub>1</sub>-C<sub>10</sub>-alkylene, isophoronylene, 2-methylpentamethylene, 2,2,4- and 2,4,4-trimethyl-1,6-hexamethylene, 1,4-cyclohexylene, 3-methylene-1-methyl-1-cyclohexylene, 2-butyl-2-ethylpentamethylene, 4-methyl-1,3-cyclohexylene, 4,4'- and 2,4'-methylenebis(cyclohexylene), xylylene, tetramethylxylylene radical or a mixture thereof and R<sup>2</sup> is a linear or branched, saturated or unsaturated alkylene or cycloalkylene radical having from 1 to 20 carbon atoms, a substituted or unsubstituted arylene radical having from 3 to 20 carbon atoms or any linear or branched sequence of two or more of the radicals mentioned which may, if desired, be linked to one another via ether, thioether, amine, amide or ester groups. Mixtures of the specified radicals R<sup>2</sup> are also possible.
- To prepare the building blocks of the present invention, diisocyanates are reacted with alcohols, thiols, primary or secondary amines or carboxylic acids to form the corresponding addition products. In the case of the reaction with carboxylic acids, this generally proceeds with elimination of CO<sub>2</sub>. Particular preference is given to the reaction of diisocyanates with alcohols, thio alcohols and amines.

- The reaction is generally carried out at from 0 to 120°C and the reaction time is usually from 5 minutes to 24 hours. The reaction is preferably carried out under protective gas with or without a solvent, if desired with addition of catalysts customary in polyurethane chemistry. Preference is given to using solvents which are inert toward isocyanate groups. Examples which may be mentioned are benzene, toluene, chlorobenzene, dichlorobenzene, diethyl ether, tetrahydrofuran, dioxane, acetone, 2-butanone, ethyl acetate, butyl acetate, chloroform, methylene chloride, N-methylpyrrolidone, dimethylformamide and dimethylacetamide.

- In a preferred embodiment, diisocyanates whose isocyanate groups have differing reactivity toward the component which is reactive toward isocyanate are used as starting materials. In this case, the building blocks of the present invention are obtained by

Particular preference is given to isocyanates having NCO groups of differing reactivity, e.g. aromatic diisocyanates such as tolylene 2,4-diisocyanate (2,4-TDI), diphenylmethane 2,4'-diisocyanate (2,4'-MDI), 3-alkyldiphenylmethane 4,4'-diisocyanate, where the alkyl radical has from 1 to 10 carbon atoms, or aliphatic diisocyanates such as isophorone diisocyanate (IPDI), 2-butyl-2-ethylpentamethylene diisocyanate, 2-isocyanatopropylcyclohexyl isocyanate, 3-isocyanatomethyl-1-methyl-1-isocyanatocyclohexane, lysine alkyl ester diisocyanate, where alkyl is C<sub>1</sub>-C<sub>10</sub>-alkyl, dicyclohexylmethane 2,4'-diisocyanate (2,4'-HMDI) and 4-methylcyclohexane 1,3-diisocyanate (H-TDI).

5 isocyanates whose NCO groups are coupled via an electronic

- 15 diisocyanate, xylylene diisocyanate, diphenylmethane

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25 and diisopropanolamine has one NCO group and two secondary OH groups. It can be isolated as a solid and can be stored for some time (about 24 hours) at room temperature.

30 are addition products of hexamethylene diisocyanate, isophorone diisocyanate, tetramethylxylylene diisocyanate, tolylene 2,4'-diisocyanate, diphenylmethane 4,4'-diisocyanate, diphenylmethane 2,4'-diisocyanate or p-phenylene diisocyanate and monoalcohols, for example methanol, ethanol, propanol, butanol, 35 hexanol, hexenol, octanol, decanol, dodecanol, octadecanol, octadecenol, allyl alcohol or benzyl alcohol, etherified monoalcohols such as ethylene glycol monomethyl ether, propylene glycol monomethyl ether, polyethylene glycol monomethyl ether or polypropylene glycol monomethyl ether, thio alcohols such as 40 mercaptoethanol, butanethiol or dodecanethiol, monoamines such as methylamine, ethylamine, propylamine, butylamine, dibutylamine, hexylamine, octylamine, decylamine, aniline or benzylamine, polyalkylene oxides functionalized with amino groups, monocarboxylic acids such as acetic acid, propionic acid, butyric 45 acid, hexanoic acid, octanoic acid, decanoic acid or benzoic acid, dialkanolamines such as diethanolamine, dipropanolamine or diisopropanolamine, trialkanolamines such as

5 mercaptopropionic acid, aminocarboxylic acids such as glycine,  $\beta$ -alanine or aminocaproic acid, or aminosulfonic acids such as taurine. If the acids are used in the form of their salts, preference is given to sodium, potassium or ammonium salts. Further possible building blocks are phosphorus-containing

20 If a building block of the present invention is used for functionalizing a compound or a surface which has groups which are reactive toward isocyanate, it is advantageous but not absolutely necessary to generate this building block in situ and

25 subsequently to react it with the compound or surface having groups which are reactive toward isocyanate. The choice of the isocyanate and the molecular fragment  $-(Y)_n$  of the isocyanate-reactive compound of the formula 3 is made according to the properties which the compound or surface having

30 isocyanate-reactive groups is to have after functionalization or modification with the building blocks.

The functionalization or modification of a compound or a surface is carried out by bringing the NCO-containing building blocks of the present invention, either in pure form or in a solvent, into contact with the compound or surface to be functionalized or modified. The reaction between the NCO groups of the building blocks of the present invention and the NCO-reactive groups of the compound or surface to be functionalized or modified preferably takes place at from 0 to 120°C for reaction times of from 5 minutes to 24 hours, if desired with addition of catalysts. Here, the building blocks of the present invention can also be used in a substoichiometric amount, based on the functional groups of the substrate to be functionalized or modified, in order to carry out, if desired, a partial modification of the compound or the surface.



5 monomers are OH- or NH-containing substances such as ethylene glycol, propylene glycol, butanediol, pentanediol, hexanediol, glycerol, trimethylolpropane, pentaerythritol, sorbitol, sugar, ethylenediamine, butylenediamine, hexylenediamine or melamine. Examples of polymers are OH-containing polymers such as polyether  
0 polyols, polyester polyols, polyacrylate polyols, polyvinyl alcohols, polybutadiene alcohols, NH-containing polymers such as amino-terminated polyetherols, polyalkylenimines, polyalkyleneamines, polyvinylimidazoles, polyamidoamines and polymers containing acid or acid anhydride groups, e.g.  
5 polyacrylic acids or polymers containing maleic anhydride groups.

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25 functionalized by, for example, hydroxy, amino, carboxy, thiol or NCO-reactive silane groups.

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The invention is illustrated by the examples below.

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subsequently allowed to react for another 60 minutes at 80°C. The molar ratio of isocyanate to the alcohol was 1:1. Apart from unreacted diisocyanate, the diadduct was formed as by-product, but this could, if desired, be removed by purification operations (chromatography, crystallization). The data for product 4 are shown in Table 1.

Table 1: OH-components as reactants

Product No.	Isocyanate	Alcohol	NCO content (% by wt.)	Properties
1	HDI	Octadecanol	9.6	Melting point: 57 - 58 °C
2	HDI	cis-9-Octadecen-1-ol	9.6	Melting point: 28 - 31 °C
3	HDI	Hydroxyethyl methacrylate	14.1	Viscosity at 23°C, 80% in ethyl acetate: 77 mPas
4	TDI	Hydroxyethyl acrylate	14.5	Melting point: 38 - 40°C

HDI = Hexamethylene 1,6-diisocyanate  
TDI = Tolyene 2,4-diisocyanate

### 1.3. Monothiourethane derived from isophorone diisocyanate (IPDI)

222 g of IPDI (1 mol) were placed in a reaction vessel under a blanket of nitrogen and heated to 50°C. At this temperature, 1 mol of mercaptoacetic acid dissolved in 200 ml of dry chlorobenzene was added dropwise over a period of 30 minutes. The mixture was allowed to react for another 60 minutes at 50°C. The addition product was preferably not purified or isolated, but reacted directly with the molecules or surfaces to be modified or functionalized. The data for the product 5 are shown in Table 2.

### 1.4. Monoureas derived from diisocyanates and amines or alkanolamines

1 mol of the respective isocyanate was dissolved in 300 ml of THF (dry) and cooled to 10°C. 1 mol of the appropriate amine dissolved in 100 ml of THF was subsequently added over a period of 30 minutes, with the temperature being maintained at 10°C. The mixture was stirred for another 30 minutes at 10°C. The products from TMXDI were found to be surprisingly stable and could be

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stored for some time (about 24 hours) at room temperature without polymerization. The adducts derived from IPDI were preferably not isolated, but reacted directly with the molecules or surfaces to be modified or functionalized. Data for the products 6 to 11 according to the present invention are shown in Table 2.

Table 2: Components containing SH and COOH groups or NH and OH groups as reactants

Product No.	Isocyanate	Reactive component	NCO content (% by wt.)	Purity (% by area in GPC)
5	IPDI	Mercaptoacetic acid	13.4	90.0
6	IPDI	Dodecylamine	10.3	99.0
7	IPDI	Isopropanolamine	14.1	91.0
8	IPDI	Diisopropanolamine	11.8	99.0
9	TMXDI	Diethanolamine	12.0	89.0
10	TMXDI	Diisopropanolamine	11.1	96.0
11	TMXDI	Tris(hydroxymethyl)-aminomethane	11.5	91.0

IPDI = Isophorone diisocyanate

TMXDI = Tetramethylxylene diisocyanate

## 2. Modification of macromolecules

2.1. Modification of a polyamine dendrimer having NH<sub>2</sub> functionality 8 as described in WO 93/14147, commercially available as ASTRAMOL® grade from DSM N.V.

The reaction product of HDI and octadecenol (monourethane 2 from Table 1) and dry THF were placed in a reaction vessel and cooled to 10°C. At this temperature, the dendritic polyamine (M = 773 g/mol) dissolved in THF was added over a period of 30 minutes, and the mixture was subsequently stirred at 23°C for another 1 hour. The amount added was calculated so that 1 mol of NH<sub>2</sub> groups of the polyamine per mol of NCO groups was reacted. The product which precipitated was filtered off, washed with THF and dried under reduced pressure at 40°C. Yield: 93% of theory, melting point 119 - 120°C.

While the polyamine dendrimer dissolved, for example, in water or ethanol, the modified product was not soluble in these. However, the modified dendrimer dissolved in, for example, chlorobenzene, n-heptane or isooctane.

## 2.2. Modification of a polyethylenimine

118 g of the reaction product of HDI and octadecenol (monourethane 2 from Table 1) and 400 ml of dry THF were placed in a reaction vessel. At room temperature (23°C), 10.5 g of polyethylenimine ( $M_n = 700$  g/mol) dissolved in 100 ml of distilled water were added over a period of 30 minutes, and this mixture was subsequently stirred at 23°C for another 4 hours. The reaction mixture was admixed with 2 l of acetone, stirred well and allowed to stand for 12 hours. The solid which precipitated was filtered off, washed with acetone and dried under reduced pressure at 40°C.

The yield was 89% of theory and the melting point was 119 - 121°C.

While the polyethylenimine dissolved in water, the modified product was insoluble therein. However, it did dissolve in, for example, chlorobenzene or butyl acetate.

## 2.3. Functionalization of a high-functionality polyacrylate alcohol

(Lumitol® H 136, BASF AG)

25 g of the adduct of TDI and hydroxyethyl acrylate (monourethane 4 from Table 1) was dissolved in 100 ml of dry chlorobenzene and heated to 40°C. A solution of 68.7 g of Lumitol® H 136 in 100 ml of butyl acetate was added dropwise over a period of 1 hour and the mixture was subsequently stirred at 40°C for 4 hours. After this time, IR spectroscopy no longer detected any NCO bands in the product mixture. Taking off the solvent gave a solid which contained acrylate groups and had a melting range of 31 - 35°C.

## 3. Modification of surfaces: hydrophobicization of a woven cotton fabric

Two solutions (solution 1 and solution 2) comprising 100 ml of dry tetrahydrofuran and 50 mg of dibutyltin dilaurate were prepared in parallel. 2 g of the adduct of HDI and octadecenol (monourethane 2 from Table 1) were additionally added to solution 1 and dissolved therein. A 5 x 10 cm piece of a woven cotton fabric was subsequently placed in each of the two solutions and the reaction solutions together with the fabric pieces were heated in parallel at 60°C for 2 hours. After cooling, the woven cotton fabrics were taken from the solutions, each washed with 2 x 100 ml of tetrahydrofuran and dried completely by means of a hot air blower. The fabrics were subsequently wetted with water. While the untreated fabric from solution 2 became fully soaked by

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the water, the water all ran off in beads from the monourethane-modified fabric.

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